

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

1,082,568



PATENT SPECIFICATION

NO DRAWINGS

1,082,568

Date of Application and filing Complete Specification: May 13, 1965.
No. 20253/65.

Application made in Germany (No. N24996 Vla/40b) on May 16, 1964.
Complete Specification Published: Sept. 6, 1967.
© Crown Copyright 1967.

Index at acceptance:—C1 A(E2G, G32, G34, G37, G38, G40, G41, G52); C7 A(A33Y, A34Y, A37Y, A39Y, A41Y, A44Y, A53Y, A68Y, A682, 72Y); C7 D(8H, 8S, 8U, 8W, 8Y, 8Z2, 8Z5, A1)

Int. Cl.:—C 22 c 29/00

COMPLETE SPECIFICATION

Improvements relating to Mouldings of Carbides

We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, E.C.2, a British Company, do hereby declare the invention, for

5 which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to mouldings of a carbide of a metal selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum, and tungsten, or a mixture of two or more of these carbides, by pressure-sintering with the use of an auxiliary metal which

15 promotes sintering.

The above-mentioned carbides and mixed carbides are of considerable technical importance owing to their high melting point, metallic conductivity, hardness, and chemical resistance. The manufacture of mouldings from pure powdered carbides is very difficult technically. Metallurgical methods, in which the material is melted, are not practicable owing to the high melting points of these carbides. Sintering the pure powdered carbides without pressure yields bodies which are not sufficiently dense for many applications.

The known pressure-sintering method, which uses the simultaneous application of heat and pressure, has been used to manufacture mouldings of pure powdered carbides with a minimum porosity, but the temperatures and pressures necessary to produce such mouldings are very high. It is desirable for production purposes to work at rather lower temperatures and pressures than those hitherto required to produce mouldings of pure powdered carbides which have a low por-

osity.

When a metal selected from iron, cobalt, nickel and manganese is added to a metal carbide for example, tantalum carbide, niobium carbide or tungsten carbide, the increase in density of the powdered carbide is strongly accelerated during sintering or pressure-sintering. It is notable that even very small quantities, for example, 0.02% by weight of Fe added to TaC, can be sufficient to obtain densities of the sintered product which approach the theoretical density calculated from X-ray data, when the pressure-sintering is conducted at comparatively low temperatures, for example 0.5 T_s, where T_s is the melting-point in degrees absolute of the hard substance.

The present invention provides a method of manufacturing a moulding from a powder of a carbide of a metal selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum and tungsten, comprising the steps of mixing the powder with an auxiliary metal which promotes sintering of the powder and then pressure-sintering the mixture, wherein the auxiliary metal is a metal or an alloy of two or more metals selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and rhenium, and wherein the quantity of auxiliary metal in the mixture is from 0.1% to 3.0% by weight of the carbide. The powder may consist of a mixture of two or more of the said carbides. In Tables I and II, a few results are given of the pressure sintering of TaC and other carbides. The specific surface of the carbide powders used was approximately between 0.3 and 0.5 square metres per gram.

40

45

50

55

60

65

70

75

TABLE I

Example No.	Addition	% by wt. of addition	Sintering temperature °C.	Product density as % of theoretical density
1	Ru	1	2,000	98.6
2	Rh	1	2,000	95.2
3	Pd	1	1,800	99.0
4	Os	1	2,400	97.0
5	Ir	1	2,150	98.5
6	Pt	1	1,600	96.2
7	Pt	1	1,800	97.5
8	Re	1	2,100	87.5
9	Re	1	2,500	91.7
10	none	—	2,000	57.0
11	none	—	2,400	82.0
12	none	—	2,500	88.0

The carbide used in Examples 1 to 12 was tantalum carbide and during the pressure-sintering process, a pressure of 300 atmospheres was applied for 60 minutes in each case. 5

TABLE II

Example No.	Carbide	Addition	% by wt. of addition	Sintering temperature °C.	Density of Product	Density as % of theoretical	A
13	WC	Pd	0.76	1,600	14.44	99.7	68
14	TiC	Pd	2.44	1,600	4.75	96.3	—
15	VC	Pd	2.06	1,800	5.60	96.4	70
16	ZrC	Ru	1.84	2,000	5.99	89.0	62
17	NbC	Pd	1.53	2,200	6.90	87.9	80
18	TaC/HfC (80:20) molar	Pd	0.85	2,000	13.54	96.0	67
19	TaC/ZrC (80:20) molar	Pd	0.94	2,000	12.46	97.2	45

In Examples 13 to 19, a pressure of 300 atmospheres was applied for 60 minutes during the pressure-sintering process. The amount of the addition in each example listed in Table II was 1% by volume of the carbide powder. The figures in the column headed A in Table II are given for comparison and are values of the density of the product expressed as percentages of the theoretical density, of carbides which have been pressure-sintered without any addition under the same conditions as were used to process the carbides with additions.

The above values of the density of the sintered product demonstrate the utility of the said auxiliary metals as materials for the promotion of sintering. In addition to the enhanced density of the product, it was found that bodies made by pressure-sintering a carbide of one of the above-mentioned metals together with an auxiliary metal were resistant to attack by a series of strong acids, when immersed in such an acid for several hours continuously. It was found that a mixture of HF and HNO₃, in a ratio of 1:1 by volume resulted in only a slight attack.

Rhenium and osmium may be used as the auxiliary metal when the mouldings are to be used at high temperatures, on account of the low volatility of these two metals.

It was found that a technically useful acceleration of the density promotion process is obtained when the quantity of the auxiliary metal used is sufficient to coat the carbide powder with a monatomic layer. For the distribution and the packing density of the auxiliary metal atoms, the conditions were idealised.

A lower and an upper limit can be indicated for the amount of auxiliary metal during pressure-sintering of carbides. The lower limit is determined by the value of the specific surface of the powder and by the specific weight or the atomic weight of the auxiliary metal in the above described manner. It should be noted that the idealised conditions with respect to the packing density and the distribution of the auxiliary metal on the carbide powder do not correspond to reality. Experience has proved that from 10 to 20 times the minimum quantity of auxiliary metal constitutes a sufficient amount in substantially all cases. Consequently, for determining the upper limit when the specific surface of the carbide is known, taking into account the diameter of

the atoms in the auxiliary metal, the quantity must be calculated which is required for coating the powder with a monatomic layer. This minimum quantity must be multiplied by a factor of from 10 to 20. An optimum amount of the auxiliary metal to be used in a particular case can then be determined experimentally.

In the case of a powder with a specific surface of 0.35 square metres per gram, for example, the following values were obtained when adding Pt; the minimum quantity required for a monatomic coating was 0.146% by weight. So the optimum dosage is from 1.5% to 3.0% by weight.

When adding ruthenium the following values are obtained for a powder with the same specific surface:

minimum amount 0.103% by weight.
optimum amount 1.0% to 2.0% by weight.

The minimum quantities of auxiliary metal used which are indicated above mean the lower limit for activation of the pressure-sintering process in a technical sense. The process is in fact measurably activated by considerably smaller quantities than these minimum quantities.

WHAT WE CLAIM IS:—

1. A method of manufacturing a moulding from a powder of a carbide of a metal selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum and tungsten, comprising the steps of mixing the powder with an auxiliary metal which promotes sintering of the powder, and then pressure-sintering the mixture, wherein the auxiliary metal is a metal or an alloy of two or more metals selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and rhenium, and wherein the quantity of auxiliary metal in the mixture is from 0.1% to 3.0% by weight of the carbide.

2. A method as claimed in Claim 1, and substantially as herein described with reference to any of Examples 1 to 9 and 13 to 19.

3. A moulding of a metal carbide manufactured by a method as claimed in Claim 1 or Claim 2.

T. D. THREADGOLD,
Chartered Patent Agent,
Century House,
Shaftesbury Avenue, London, W.C.2,
Agent for the Applicants.